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Mo L-edge and S K-edge X-ray absorption spectroscopy were applied to investigate the charge distribution between Mo and S in a series of Mo thiolate compounds, which serve as amide-sulfur H-bonding models and exhibit different redox potentials arising from polar group effects and ligand hydrogen bonds near the redox center. For all oxidized complexes, the S K-edge spectra exhibit a thiolate-based pre-edge feature centered at 2470.2 eV and the inflection point occurs at 2472.0 eV. No intense pre-edge feature is observed in the spectra for the reduced Mo model compounds and the energy shift of the S K-edge position depends on the S-ligand. Correlations between ligand charge density and the redox potential of the Mo-S cores are observed.

Keywords: S K-edge, pre-edge, XAS, redox potential, hydrogen bonding

1. Introduction

The effect of hydrogen bonding and polar group effects on redox potentials in cysteine-metal electron-transfer proteins has been the subject of extensive discussion over the course of nearly two decades. The nature of the electronic structure of these metal-sulfur active sites and their relationship to electron transfer is not yet understood, however, the ligand-metal interactions seem to play an important role. A quantitative description of the charge distribution between metal and ligand is necessary to define the contribution of ligand-metal bonding to the reduction potentials of the active sites. A powerful tool to investigate the charge distribution in Mo-S compounds is Mo L-edge in combination with S K-edge X-ray Absorption Near Edge Spectroscopy (XANES).

In this paper we report S K-edge and Mo $L_{2,3}$-edge spectra for a set of alkanethiolate complexes $Mo[HB(Me_2pz)_3](NO)(SR)_2$ with (pz = pyrazole) and R = Et (**1**), Bu (**2**), $CH_2CONHCH_3$ (**3**), $CH_2CON(CH_3)_2$ (**4**), $C_2H_4CONHCH_3$ (**5**), and $C_2H_4CON(CH_3)_2$ (**6**) (Huang *et al.*, 1994; Huang *et al.*, 1993) that are well suited to study the effect of polar groups and ligand hydrogen bonds in the proximity of the redox center (Fig. 1). The simple alkylthiolate complexes (**1**) and (**2**) serve as controls and reside close together at the low end of the redox potential scale with couples in $CHCl_3$ solution at -1.008 and -0.968 V (relative to Ag), respectively. Compounds **4**, **5** and **6** show a positive redox shift of +300 mV, in $CHCl_3$ relative to **1** and **2**. N-H···S hydrogen bonds are absent in **4**, **5** and **6**. Huang *et al.* (1994) have demonstrated that these positive shifts appear because the polarity of the environment adjacent to the redox active site has a strong influence on the redox potential, similar in magnitude and direction to the effect of ligand hydrogen bonding. At the high end of the scale is compound **3**, in $CHCl_3$, with a redox couple of -0.563 V. The positive shift of 450 mV found for **3** (Huang *et al.*, 1994), relative to the alkylthiolates was congruent with the results of several other studies that suggested that N-H···S hydrogen bonding in Fe-S complexes is accompanied by positive redox potential shifts (Ueyama *et al.*, 1985; Nakata *et al.*, 1984). This set of model compounds, which exhibit structural and spectroscopic characteristics very similar to metalloproteins, are very well suited to study the charge distribution between the metal (Mo) and the ligand (N_{pz}, NO, S) in the oxidized and reduced compound. The investigation of these compounds will give us a better understanding of, where the charge density is deposited upon reduction, and how the S K-edge position can be correlated with the redox potential.

2. Experimental Section

The S-ligands NaSEt, NaSBu, $NaSCH_2CONHCH_3$, $NaSCH_2CON(CH_3)_2$, $NaSC_2H_4CONHCH_3$ and $NaSC_2H_4CON(CH_3)_2$ and the molybdenum alkanethiolate complexes $Mo[HB(Me_2pz)_3](NO)(SR)_2$ with (pz=pyrazole) and R = Et (**1**), Bu (**2**), $CH_2CONHCH_3$ (**3**), $CH_2CON(CH_3)_2$ (**4**), $C_2H_4CONHCH_3$ (**5**), and $C_2H_4CON(CH_3)_2$ (**6**) were prepared as described before (Huang *et al.*, 1994). The corresponding reduced compounds, **1′**–**6′**, were made by following published procedures. Compounds **1′** and **2′** were made by a controlled-potential reduction (Hill *et al.*, 1977) with a standard three-electrode cell. Compounds **3′**–**6′** were made following procedures of Cook *et al.* (1993) and Maher *et al.* (1994) using cobaltocene ($Co(C_5H_5)_2$).

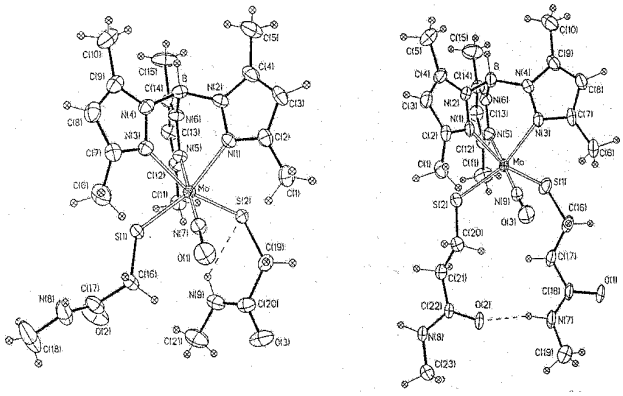

Figure 1
Crystal structures of **3** and **5,** adapted from Huang *et al.* (1994).

S K-edge and Mo $L_{2,3}$-edge spectra were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL) using the 54-pole wiggler beamline 6-2, with a Pt-coated focusing mirror and a Si(111) double crystal monochromator. Details of the setup and sample preparation have been described earlier (Shadle *et al.*, 1995; Rompel *et al.*, 1998). Air sensitive compounds were ground in an argon-filled glovebag and covered with a polypropylene window before transfer to the helium filled sample chamber. The standard

$Na_2S_2O_3 \cdot 5H_2O$ was run periodically for energy calibration purposes (pre-edge position = 2472.02 eV).

To analyze the data, we followed a procedure similar to that used before (Rompel *et al.*, 1998). Normalization of the spectra was accomplished by fitting a quadratic function to the data in the far post-edge region and extrapolating to the energy of the first absorption maximum, where the absorbance was set to unity. The pre-edge position for each S K-edge spectrum were determined from the energy of the zero-crossing of the first derivative. The first inflection-point energy of the steeply rising absorption edge was determined from the zero-crossing of the second derivative of the spectrum. Analytical differentiation of a third-order polynomial fit to the data over an interval of 1.5 eV on each side of a data point produced the derivative spectra. Since the molybdenum L_3-edge is only ≈ 50 eV higher in energy than the S K-edge, the S K-near edge structure is superimposed upon the edge structure of the molybdenum L_3-edge. In these cases, lines were fitted to either the pre- or the post-edge regions and subtracted.

3. Results and Discussion

We studied this set of molybdenum alkanethiolate complexes in their oxidized $Mo[HB(Me_2pz)_3](NO)(SR)_2$ and reduced $[Bu_4N][Mo(HB(Me_2pz)_3](NO)(SR)_2$ form with pz = pyrazole and R = Et (**1**), Bu (**2**), $CH_2CONHCH_3$ (**3**), $CH_2CON(CH_3)_2$ (**4**), $C_2H_4CONHCH_3$ (**5**) and $C_2H_4CON(CH_3)_2$ (**6**) by Mo $L_{2,3}$-edge and S K-edge X-ray absorption spectroscopy.

Mo $L_{2/3}$-edge

The Mo L_3- and Mo L_2-edges for the oxidized and reduced Mo-thiolate compounds were recorded. The prominent feature in the spectrum is the intense white line assigned to the allowed $2p \rightarrow 4d$ transitions. For all oxidized compounds, the white line is split into two transitions. The top of the edge position also stays within 0.1 eV, which demonstrates that the effective charge on the Mo is not significantly different for all oxidized compounds independent of the thiolate ligand (Table 1). The same trend is observed at the Mo L_2-edge, where the two rising edge inflection point energies as well as the top of the edge stays within 0.1 eV.

Upon reduction, the shape of the Mo L_3-edge and Mo L_2-edge changes. All reduced compounds exhibit a single band (with a small shoulder). The $L_{2,3}$-edges of the reduced compounds show a shift in the inflection point energy compared to the oxidized compounds. Because of the dramatic changes in edge shape upon reduction, it seems to be more appropriate to compare the top of the edges than the IPE energies. For the reduced Mo-thiolates, the top of the Mo L_3-edge is shifted 0.2–0.4 eV to lower energies. A consistent decrease of 0.4–0.6 eV per unit oxidation step is found as the formal oxidation state decreases within a similar coordination geometry (Hedman *et al.*, 1988). These shifts reflect a change in the effective charge of molybdenum and let us draw the conclusion that upon reduction part of the charge is taken up by the molybdenum central atom.

S K-edge XAS

The S K-edge spectra of the oxidized molybdenum model compounds are shown in Fig. 2 as solid lines. The sulfur K-edge XANES is characterized by a white line feature, which derive primarily from a $1s \rightarrow 4p$ transition (Shadle *et al.*, 1995). Additionally, the spectra for all oxidized complexes exhibit an intense thiolate-based pre-edge feature due to a $1s \rightarrow 3d$ transition, which is centered at 2470.2 eV for **1**, **2**, **5** and **6** and 2470.3 eV for **3** and **4**. The inflection point energy and pre-edge peak energy values are summarized in Table 1. The energies for the pre-edge features for this series of Mo(III) compounds appear almost at the same positions (2470.2 and 2470.3 eV). This may indicate that the respective sulfur 1*s* core orbital energies of this complexes are the same, or it may indicate that the difference between the sulfur 1*s* and the Mo *d*-derived orbital energies are the same for this set of compounds. In contrast to the oxidized Mo model compounds, no intense pre-edge feature is observed in the spectra of the reduced ones. The dramatic intensity decrease for the first transition at 2470 eV upon reduction has been seen before for the reduced compound $Mo_2Fe_6S_8(OCH_3)_3(SC_6H_5)^{5-}$.

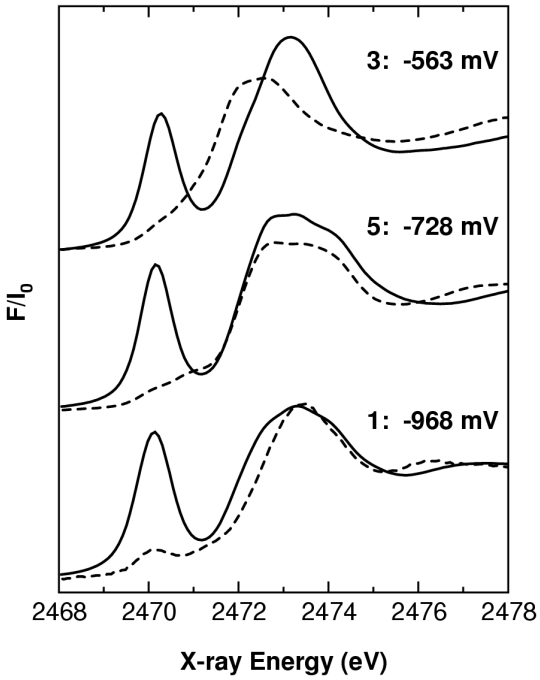

Figure. 2
Normalized S K-edge XANES spectra of oxidized $Mo[HB(Me_2pz)_3](NO)(SR)_2$ and the reduced compound $[Bu_4N][Mo(HB(Me_2pz)_3](NO)(SR)_2$ form with (pz = pyrazole) and R = Et (**1**), Bu (**2**), $CH_2CONHCH_3$ (**3**), $CH_2CON(CH_3)_2$ (**4**), $C_2H_4CONHCH_3$ (**5**) and $C_2H_4CON(CH_3)_2$ (**6**). The oxidized Mo(III)-thiolate spectra are shown in solid lines (—), the reduced Mo(II)-thiolate spectra in dashed lines (---).

The inflection point of the rising edge is 2472.0 eV for **1**, **2**, **4**, **5**, **6** and 2472.1 eV for **3**. The rising edge inflection point stays within 0.1 eV, which demonstrates that the covalency in the Mo-S interaction and the charge on S is the same for all oxidized compounds. S donates the same charge to Mo in the oxidized complexes, although these compounds exhibit different redox potentials. Besides the decrease of the pre-edge peak position, there is a energy shift for the S K-edge position dependent on the S-ligand of the reduced compounds (see Fig. 2). The overall shift in the S K-edge position is 1.1 eV for the reduced compounds, compared to 0.1 eV in the oxidized compounds. For the reduced Mo thiolate alkenes **2′** and **1′** – compounds with the lowest redox potential (see Table 1), the S K-edge appears at 2472.8 and 2472.5 eV, respectively. This position is found at an even higher energy than the energy position of their oxidized forms. For **5′**, **6′** and **4′** the S K-edge position occurs at 2472.0 eV. This is the IPE value that all oxidized compounds exhibit. **3′** shows an even lower S K-edge position of 2471.8 eV, meaning that the S in **3′** has taken up more negative charge than the other compounds. The here observed trend between the redox potential and the charge on the S is shown as a correlation between the S K-edge inflection point and the redox

Table 1
Mo L-Edge Rising Edge Inflection Points and S K-Edge Pre-Edge Energies and Rising Edge Inflection Points for the Reduced and Oxidized Molybdenum Alkanethiolates.

Compounds	Mo L_3-edge top[†] [eV]	Mo L_2-edge top[†] [eV]	S K-pre-edge Position[†] [eV]	S K-edge inflection[§] [eV]	Redox Potential [V]
$Mo^{III}[HB(Me_2pz)_3](NO)(SR)_2$					
SBu (**2**)	2525.8	2630.3	2470.2	2472.0	-1.008
SEt (**1**)	2525.8	2630.3	2470.2	2472.0	-0.968
$SC_2H_4CONHCH_3$ (**5**)	2525.8	2630.3	2470.2	2472.0	-0.728
$C_2H_4CON(CH_3)_2$ (**6**)	2525.9	2630.4	2470.2	2472.0	-0.710
$CH_2CON(CH_3)_2$ (**4**)	2525.8	2630.3	2470.3	2472.0	-0.713
$CH_2CONHCH_3$ (**3**)	2525.9	2630.4	2470.3	2472.1	-0.563
$[Bu_4N]Mo^{II}[HB(Me_2pz)_3](NO)(SR)_2$					
Bu (**2**)	2525.5	2630.1		2472.8	
Et (**1**)	2525.5	2630.1		2472.5	
$C_2H_4CONHCH_3$ (**5**)	2525.6	2629.9		2472.0	
$C_2H_4CON(CH_3)_2$ (**6**)	2525.5	2629.9		2472.0	
$CH_2CON(CH_3)_2$ (**4**)	2525.6	2629.9		2472.0	
$CH_2CONHCH_3$ (**3**)	2525.5	2629.9		2471.8	

[†]The precision of these energies is < ±0.05eV.

[§]The precision of the inflection point energy is < ±0.1 eV; the inflection point reported is determined from the zero-crossing of the second derivative of the spectrum.

potential. Further studies will include comparing these data with those of the oxidized and reduced compounds in frozen solution.

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